

THE IMPORTANCE OF GRAND CANYON CAVES AND MINES TO THE EVOLUTION OF THE COLORADO RIVER SYSTEM

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INTRODUCTION

Caves in the Grand Canyon are important to understanding the geologic evolution of the Colorado River System because they preserve – in their mineralogic and geologic features – a record of events during the Late Tertiary. Similarly, certain minerals exposed in the mines of the Grand Canyon may also preserve a record of the descent of the regional water table, and thus constrain the age of down cutting of the Grand Canyon.

Our study, "The Origin and Timing of Ore Mineralization and Cave Development in the Grand Canyon" is just beginning; therefore, the interpretations set forth in this abstract and in our Symposium poster paper should be considered as preliminary. However, while preliminary, the results achieved so far are both interesting and encouraging. For a more detailed discussion of this project, refer to the unpublished reports of Hill and others (1998, 1999, 2000) to Grand Canyon National Park.

MINES

Mines visited so far during this study are: the Grandview mine, Kaibab trail barite site, the Riverview mine, the Anita mines (Copper Queen mine, Northstar prospects, Emerald mine, Eastern Star prospects), and the Ridenour mine. The expected sulfide (primarily chalcocite) and secondary copper (e.g., azurite, malachite) mineralization was encountered in these mines, but in addition the minerals alunite, endellite (hydrated halloysite), hydrobasaluminite, and illite were found in the Grandview mine, and illite, with chlorite, was found at the Riverview mine.

The importance of alunite [$K_2Al_6(SO_4)_4(OH)_{12}$] is two-fold. First, because alunite contains potassium, it can be dated by the $^{40}Ar/^{39}Ar$ method. Second, four different stable isotope values can be determined on this one mineral – sulfur on the SO_4 , hydrogen on the OH, oxygen on the OH, and oxygen on the SO_4 . These stable isotope values not only can be used to differentiate between supergene and magmatic alunite, but they can also indicate the temperature and character of the mineral-forming water (Rye and others, 1992). The $^{40}Ar/^{39}Ar$ date obtained on the Grandview alunite (at the New Mexico Geochronology Lab, Socorro) was ~700 Ka. The stable isotope values obtained on the Grandview alunite (by Robert Rye at the USGS) was $\delta^{34}S = -7.4\text{‰}$, $\delta D = -85\text{‰}$; and $\delta^{18}O_{(SO_4)} = 6.7\text{‰}$, $\delta^{18}O_{(OH)} = 9.3\text{‰}$, with a $\delta SO_4-OH = -2.6\text{‰}$. The importance of this isotopic data to the history of the Colorado River System is that it implies that the alunite in the Grandview mine formed at a low temperature at or just below the water table at about 700,000 YBP. This is in contrast to past studies which have placed the canyon bottom near its present location for the past ~1.5 Ma based on K-Ar dating of basalts. The elevation of the Grandview mine on Horseshoe Mesa is about 4500 ft (1370 m), and the elevation of the Colorado River in that part of the Canyon is about 2400 ft (730 m) – a drop in the water table of about 2100 ft (640 m) in ~700,000 yrs, or ~1 mm/yr (assuming a relatively flat water table and not taking into account fault displacement).

The Grandview mine endellite and hydrobasaluminite are important because both are sulfuric acid minerals, formed from the oxidation of sulfides and subsequent alteration of clays (Hill, 1990; Polyak and others, 1998). Illite collected from the Grandview mine, and also illite from the Riverview mine – which supposedly formed during the ore mineralization episode by the argillic alteration of kaolinite to illite (Barrington and Kerr, 1963) – are now being dated by $^{40}Ar/^{39}Ar$ at the New Mexico Geochronology Lab, Socorro. These dates on illite may help determine the timing of the ore mineralization episode.

CAVES

Caves visited so far during this study are: Cave of the Domes, Tse'an Bida, Tse'an Kaetan, and Grand Canyon Caverns. All of these caves are developed in the Mooney Falls Member of the Redwall Limestone, and all contain replacement gypsum rinds or blocks such as exist in the caves of the Guadalupe Mountains, New Mexico (e.g., Carlsbad Cavern and Lechuguilla Cave; Hill, 1990). The results of the sulfur isotope analyses performed on the cave gypsum are shown in Figure 1. As determined by these analyses, the cave gypsum is *speleogenetic* in origin – that is, it formed by a sulfuric acid reaction at or near the water table and is not *speleothemic* gypsum derived from evaporites in the overburden. Evaporites contained in Mississippian & Triassic rock have sulfur isotope values of $\delta^{34}\text{S} = +10$ to $+25\text{‰}$ (Faure, 1977; Fig. 1); therefore the cave gypsum ($\delta^{34}\text{S} = -7\text{‰} \pm 4\text{‰}$; Fig. 1) could not possibly have come from this source.

This study thus far indicates that the Redwall caves are probably H_2S - CO_2 mixing-zone caves, where deep-sourced hydrothermal water containing H_2S , CO_2 , and metals, mixed with meteoric water having a high O_2 content, but a low TDS, H_2S , and CO_2 content. The Redwall caves display this general sequence of events: (1) a hematitic-Mn rich layer (enriched in As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V, Zn), overlain by (2) hydrothermal calcite spar linings, overlain by (3) replacement gypsum crusts. Where upwelling H_2S , CO_2 , metal-rich water mixed with oxygenated, descending, meteoric water, the cave voids dissolved by the mixture-corrosion mechanism of Bögli (1980); then the metals precipitated within the cave voids due to the mixing of oxygenated water with metal-rich water. A decrease of temperature and CO_2 degassing at the water table caused the calcite spar linings to precipitate over the hematitic material, and H_2S degassing at or just above the water table caused gypsum to replace limestone.

If the water-table is reflected by the Grandview mine alunite date (~ 700 Ka), then the final developmental stages of Redwall caves (at least the ones in the Horseshoe Mesa area) also probably occurred ~ 700 Ka. In addition to alunite dating, U-Pb dating of the calcite-spar cave linings is another method which could provide a time constraint on water-table lowering and incision of the Grand Canyon.

HYDROCARBONS

The isotopically light sulfur isotope composition of the cave gypsum implies that the Redwall caves formed (at least in part) by a sulfuric acid mechanism related to the migration of H_2S from hydrocarbons (Hill, 1990). Although the data at this time is very preliminary, note in Figure 1 that the sulfur isotope values of the cave gypsum and Grandview mine alunite are almost identical to the native sulfur in the Walcott Member of the Chuar Group (all around $\delta^{34}\text{S} = -7\text{‰}$). Also note that the barite from the Grandview mine and Kaibab trail sites have almost identical isotopic compositions ($\delta^{34}\text{S} = +11\text{‰}$). This data may possibly reflect the uniformity of a H_2S source (hydrocarbons in the Precambrian Chuar?). Hydrocarbons are known to occur in the Redwall Limestone near Tse'an Kaetan; hopefully these can be characterized and compared with hydrocarbons in the Chuar to help verify the source of H_2S .

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REFERENCES

- Barrington, J., and Kerr, P. F., 1963, Collapse features and silica plugs near Cameron, Arizona: Geological Society of America Bulletin, v. 74, p. 1237-1258.
- Bögli, A., 1980, Karst hydrology and physical speleology: Springer-Verlag, Berlin, 284 p.
- Faure, G., 1977, Principles of isotope geology: New York, John Wiley, 464 p.
- Gornitz, V., and Kerr, P. F., 1970, Uranium mineralization and alteration, Orphan mine, Grand Canyon, Arizona: Economic Geology, v. 65, no. 7, p. 751-768.
- Hill, C. A., 1990, Sulfuric acid speleogenesis of Carlsbad Cavern and its relationship to hydrocarbons, Delaware Basin, New Mexico and Texas: American Association of Petroleum Geologists, v. 74, no. 11, p. 1685-1694.
- Hill, C. A., 1997, Geology of the Delaware Basin – Guadalupe, Apache, and Glass Mountains – New Mexico and West Texas: SEPM-Permian Basin Section, Publication no. 96-39, 480 p.

- Hill, C. A., Buecher, R., Buecher, D., Mosch, C., and Goar, M., 1998, Trip Report — Horseshoe Mesa, March 14-16, 1998: Unpublished Report to Grand Canyon National Park, August, 1998, 34 p.
- Hill, C. A., Polyak, V. J., Buecher, R., Buecher, D., Provencio, P., and Hill, A., 1999, Trip Report — Tsean-Bida Cave and Riverview mine, March 19-21, 1999, and Kaibab trail barite locality, November 18, 1998; Unpublished Report to Grand Canyon National Park, September, 1999, 68 p.
- Hill, C. A., Polyak, V. J., Buecher, D. C., Buecher, R. H., and Provencio, P. P., 2000, Trip Report – Tse'an Kaetan (Cave of Prayer Sticks), Grand Canyon, Arizona; Unpublished Report to Grand Canyon National Park, February, 2000, 46 p.
- Miller, D. S., and Kulp, L., 1963, Isotopic evidence on the origin of Colorado Plateau uranium ores: Geological Society of America Bulletin, v. 74, p. 609-630.
- Polyak, V.J., McIntosh, W. C., Güven, N., and Provencio, P. P., 1998, Age and origin of Carlsbad Cavern and related caves from $^{40}\text{Ar}/^{39}\text{Ar}$ of alunite: Science, v. 279, p. 1919-1922.
- Rye, R. O., Bethke, P. M., and Wasserman, M. D., 1992, The stable isotope geochemistry of acid sulfate alteration: Economic Geology, v. 87, no. 2, p. 225-262.

SULFUR ISOTOPE DATA FOR GRAND CANYON DEPOSITS

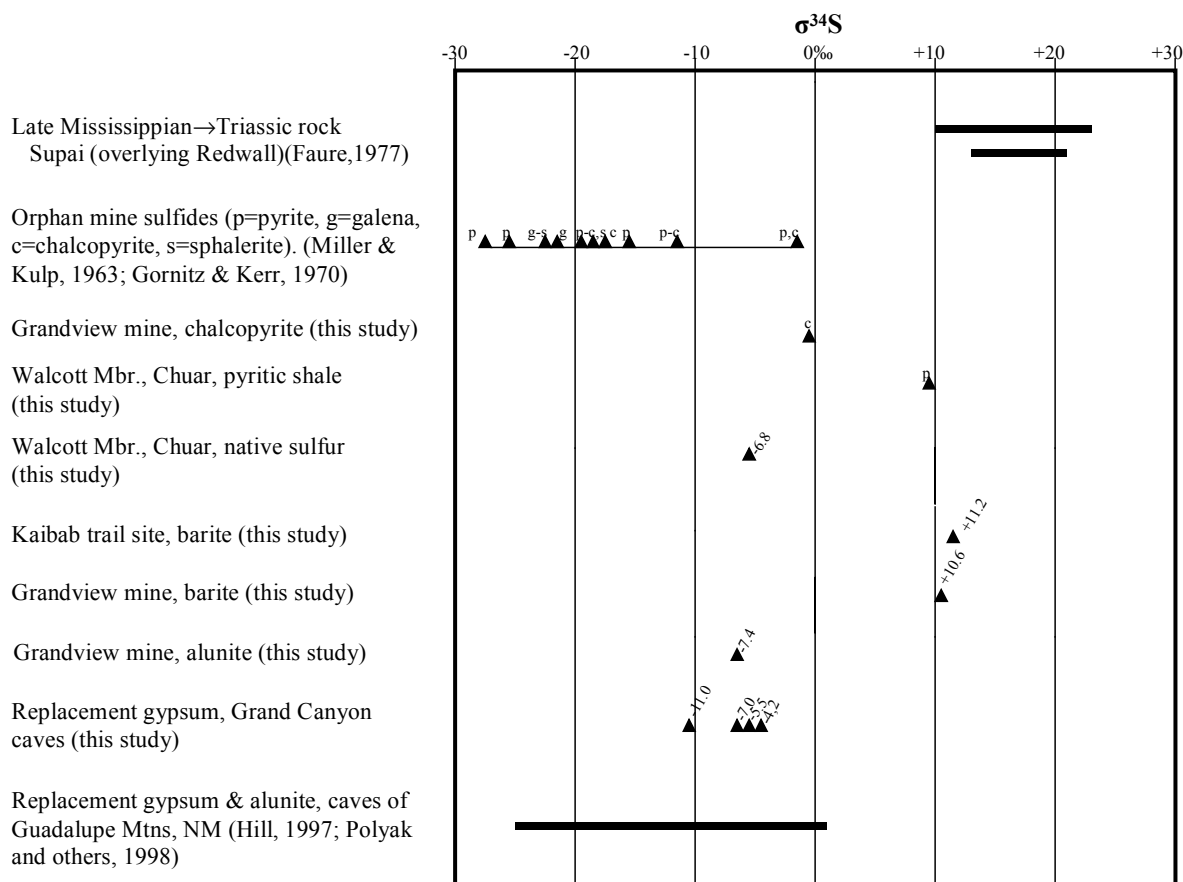


Figure 1. Sulfur isotope values for various types of deposits in the Grand Canyon. Note that: (1) the cave gypsum could not possibly have derived from evaporites in overlying Mississippian-Triassic rock; instead, the negative values imply a hydrocarbon source; (2) the unusually narrow range of values in Grand Canyon caves as compared to those in the Guadalupe Mountains, implying a uniform H_2S source; (3) the cave gypsum, the Grandview alunite, and Walcott sulfur all have $\delta^{34}\text{S}$ values $\approx -7\text{‰}$, and the two barite sites have $\delta^{34}\text{S}$ values $\approx +11\text{‰}$ – which uniformity also suggests a common source of H_2S for these sites.